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# Rotational Sublevels of an Ortho-Hydrogen Molecule Encapsulated in an Isotropic C<sub>60</sub> Cage

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From specific heat measurements in high quality H<sub>2</sub>@C<sub>60</sub> samples performed over a broad temperature range, we obtain the smallest yet observed splitting of rotational energy sublevels of encapsulated single H<sub>2</sub> molecules, 0.1–0.2 meV, in the nearly spherical potential well provided by highly isotropic C<sub>60</sub> cages. Additionally, we find evidence of the quantized oscillation state of isolated H<sub>2</sub> in the C<sub>60</sub> cage. The minuscule splitting indicates that H<sub>2</sub>@C<sub>60</sub> provides unprecedented opportunities to study free-molecule quantum dynamic properties.

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Molecular hydrogen (H<sub>2</sub>), the simplest system among all molecules, has been studied extensively to date [1–3], and its electronic spectra have been fundamental in establishing the fundamentals of quantum mechanics. An H<sub>2</sub> molecule is not expected to be completely localized at lattice sites even in the solid state at 0 K due to its large zero point motion. H<sub>2</sub> retains translational freedom as a translational quantum solid [1]. The rotational motion of the H<sub>2</sub> molecule also persists, and thus an H<sub>2</sub> crystal is also an orientational quantum solid [1]. The unique free-rotor description is a result of the nuclear spin isomers denoted by para-H<sub>2</sub>  $J = 0, 2, 4$  and ortho-H<sub>2</sub>  $J = 1, 3, 5 \dots$ , where  $J$  is the rotational quantum number. Because of wave-function symmetry requirements, the conversion between these spin isomers is forbidden, and, therefore, the energetically higher  $J = 1$  state remains an angular momentum degree of freedom down to 0 K. Indeed, the rotational motion in solid H<sub>2</sub> can be described as a nearly three-dimensional free rotor where the rotational motion is barely disturbed by the neighboring hydrogen molecules. The small interaction originating from the neighboring molecules is still a central issue in the experimental research of solid H<sub>2</sub> because these interactions can drastically modify the ortho-para conversion, crystal structure, and rotational and translational spectra [1].

Fullerene encapsulated H<sub>2</sub> molecules (H<sub>2</sub>@C<sub>60</sub>) have been only recently macroscopically synthesized by organic reactions known as the “molecular surgery method” [4] and offer an unprecedented opportunity to study the rotational and translational states of the H<sub>2</sub> molecule. The molecular dynamics of endohedral H<sub>2</sub> have recently been studied by nuclear magnetic resonance [5] and inelastic neutron scattering measurements [6] by means of H<sub>2</sub>@ATOCF (ATOCF: azacyclic-thiacyclic molecule, an open cage structure of C<sub>60</sub>). The results, however, indicate that the endohedral H<sub>2</sub> in H<sub>2</sub>@ATOCF shows limited 3D

rotational freedom due to the low symmetry of open cage C<sub>60</sub>. Although infrared spectroscopy was recently used to evaluate the rotational-vibrational coupling [7], this technique is not sensitive enough to detect the fine structure of the  $J = 1$  triply degenerate rotational sublevels [8,9] that can provide direct information about the intriguing rotational states. In this Letter, we discuss the first specific heat results of 99% pure H<sub>2</sub>@C<sub>60</sub> from room temperature down to 0.085 K. An anomaly observed at  $T = 0.6$  K is attributed to the almost degenerate quantized rotational level state. The observed small 0.1–0.2 meV energy splitting between states allows us to conclude that the encapsulated H<sub>2</sub> in the C<sub>60</sub> cage can be regarded as an almost 3D free quantum rotor.

H<sub>2</sub>@C<sub>60</sub> was synthesized by organic chemical reactions by opening and closing the C<sub>60</sub> cage structure as described elsewhere [4]. Repeated column chromatography isolation was used to produce 99% pure H<sub>2</sub>@C<sub>60</sub>. In order to increase crystallinity of the H<sub>2</sub>@C<sub>60</sub> powder, the samples were repeatedly dissolved in toluene and recrystallized on a surface of a glass plate while keeping the plate temperature at ~400 K.

High resolution x-ray powder diffraction data were collected at different temperatures in the BL02B2 beam line ( $\lambda = 1.0000$  Å) at SPring-8, followed by maximum entropy method (MEM)-Rietveld refinement to analyze the crystallographic structure of the samples. Specific heat measurements were made using a thermal relaxation time method with two calorimeters for different temperature regions. From 0.085 to 5 K, a homemade calorimeter in a <sup>3</sup>He/<sup>4</sup>He dilution refrigerator was used. To obtain good thermal contact, the specimen was pressed between two plates of sapphire together with a small amount of Apiezon-N grease. The heat capacity of the sample was obtained by subtracting the contribution of the sapphire, Apiezon-N grease, and the sample cell from the total heat

capacity. The heat capacity of the sapphire plates was extremely small, and the contribution was estimated by the Debye  $T^3$  extrapolation from the data for sapphire reference standard material (NIST SRM 720). From 2 to 300 K, the specific heat was measured using a physical property measurement system (PPMS) from Quantum Design. The values of specific heat of  $\text{H}_2@C_{60}$  obtained by the two calorimeters agree in the overlapping temperature region from 2 to 5 K.

Both  $C_{60}$  and  $\text{H}_2@C_{60}$  crystals adopt a primitive cubic  $Pa\bar{3}$  symmetry having two orientational orderings at low temperatures [10]. On the basis of the intensity of the (200) peak, where the form factor of  $C_{60}$  and endohedral  $\text{H}_2$  can cancel each other, it can be concluded that an  $\text{H}_2$  molecule was encapsulated at the center inside the cage. The density maps illustrated in Fig. 1, obtained using MEM-Rietveld analyses for both  $C_{60}$  and  $\text{H}_2@C_{60}$ , show  $\text{H}_2$  in the center of the  $C_{60}$  cage.

$C_p$  data for  $\text{H}_2@C_{60}$  and  $C_{60}$  (with the same treatment for comparison) are shown as a function of temperature in Fig. 2. Two distinct anomalies were observed: one being around 260 K and the other around 0.6 K. The former transition (260 K) is the well known rotational disorder (high- $T$ , space group  $Fm\bar{3}m$ ) to rotational order (low- $T$ , space group  $Pa\bar{3}$ ) phase transition of  $C_{60}$  [10,11]. In the high-temperature regime, the  $C_{60}$  rotational barrier is smaller than the thermal energy  $k_B T$ , and  $C_{60}$  freely rotates, whereas the intermolecular interactions of hexagon-hexagon and hexagon-pentagon fusion block the  $C_{60}$  rotation leading to its lower symmetry with two preferred orientations in the low-temperature regime [10]. The same rotational phase transition temperature for both  $\text{H}_2@C_{60}$  and  $C_{60}$  implies that the rotational motion of the  $C_{60}$  cage is not affected by the endohedral  $\text{H}_2$  molecule.

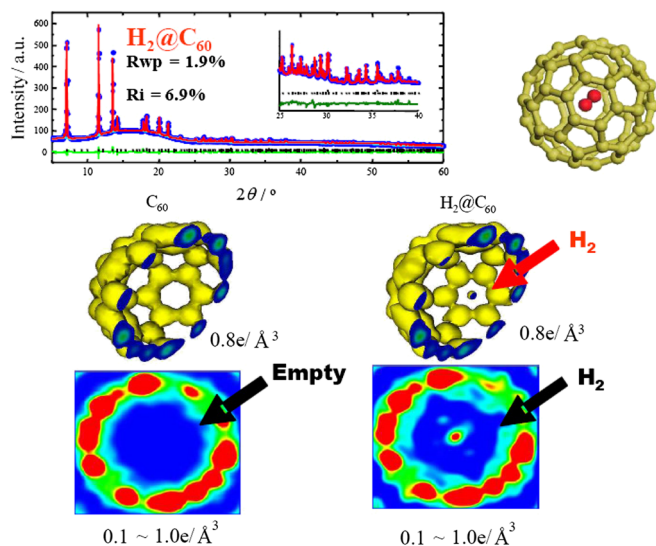


FIG. 1 (color online). X-ray diffraction pattern and electron density surface of  $\text{H}_2@C_{60}$ . The view (right side) shows that an endohedral  $\text{H}_2$  molecule locates in the center of the cage.

In Fig. 2, it is possible to see that  $C_p$  for  $\text{H}_2@C_{60}$  is larger than that for pure  $C_{60}$  over the entire temperature range. Given that the crystal structure of  $\text{H}_2@C_{60}$  is the same as that of  $C_{60}$ , it is reasonable to assume that the contribution from the  $C_{60}$  cage to the specific heat is identical for both compounds. Therefore, the difference in  $C_p$  ( $\Delta C_p$ ; excess specific heat obtained by subtracting the  $C_p$  of  $C_{60}$  from that of  $\text{H}_2@C_{60}$ ) shown in Fig. 3 is ascribed to endohedral  $\text{H}_2$ . Since  $\text{H}_2$  is a diatomic molecule, there are 6 degrees of freedom for  $\text{H}_2$ : i.e., 3 translational ( $C_{\text{trans}}$ ), 2 rotational ( $C_{\text{rot}}$ ), and 1 intramolecular vibrational ( $C_{\text{vib}}$ ) degrees of freedom. Considering that the  $\text{H}_2$  intramolecular stretching vibration frequency of  $4161 \text{ cm}^{-1}$  [1] is too high to be excited below room temperature, the excess  $\Delta C_p$  likely originates from  $C_{\text{trans}}$  and  $C_{\text{rot}}$ , i.e.,  $\Delta C_p \approx C_{\text{trans}} + C_{\text{rot}}$ .

The rotational specific heat  $C_{\text{rot}}$  is affected by the presence of ortho-para conversion. Indeed, in the presence of such conversion,  $C_{\text{rot}}$  is calculated as  $C_{\text{rot}} = d/dT\{RT^2 d/dT[\ln(0.25Z_{\text{para}} + 0.75Z_{\text{ortho}})]\}$  while, in the absence of the ortho-para conversion,  $C_{\text{rot}}$  is given by  $C_{\text{rot}} = 0.25d/dT\{RT^2 d/dT[\ln(Z_{\text{para}})]\} + 0.75d/dT\{RT^2 d/dT[\ln(Z_{\text{ortho}})]\}$ , where the participation functions  $Z_{\text{para}}$  and  $Z_{\text{ortho}}$  are  $Z = \sum (2J+1) \exp(-E_J/k_B T)$  and the rotational quantized energy levels are  $E_J = B_J J(J+1)$  [5]. If the ortho-para conversion occurs, the equilibrium specific heat ( $C_{\text{rot}}^*$ ) must show a large anomaly around 50 K as shown in Fig. 3 [12] according to the equation given earlier. In the present experiments, however, no such anomaly was observed, and therefore our results indicate that the ortho-para conversion is prohibited in  $\text{H}_2@C_{60}$ . Similar conclusions are reported in the open cage system  $\text{H}_2@A\text{TOCF}$  [5,6].

The translational motion of  $\text{H}_2$  corresponds to the oscillation of the center of mass, bound by the spherical potential created by the  $C_{60}$  framework. Similar oscillation of endohedral intercalants has been observed in other sys-

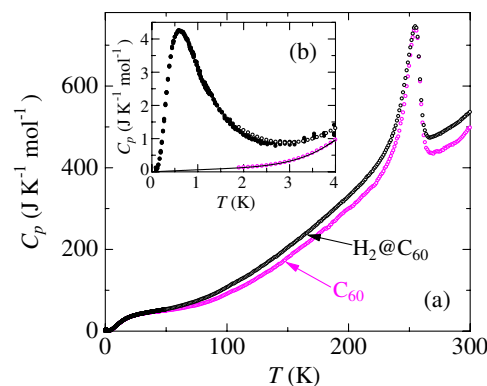


FIG. 2 (color online). Specific heat of  $C_{60}$  and  $\text{H}_2@C_{60}$ . (a) Open circles are measured by a PPMS, and solid black circles are measured by a homemade calorimeter. The solid line was obtained by extrapolation.

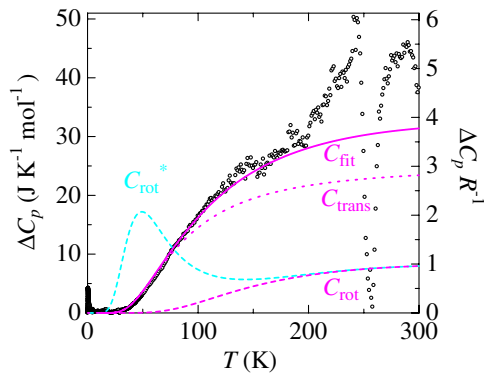


FIG. 3 (color online). Excess specific heat  $\Delta C_p$ . These data (black circles) were obtained by subtracting the  $C_p$  data of  $C_{60}$  from that of  $H_2@C_{60}$ . For the calculation below 2 K,  $C_p$  of  $C_{60}$  is estimated by extrapolation to 0 K from temperatures above 2 K [shown in Fig. 2(b)]. The magenta solid curve indicates the fitted specific heat  $C_{fit}$ , which is the summation of  $C_{trans}$  (magenta dotted curve) and  $C_{rot}$  (magenta dashed curve), while the dashed cyan curve is the rotational  $C_p$  of  $H_2$  with the equilibrium ortho-para ratio.

tems, such as clathrates and filled skutterudites, where the translational specific heat originating from the endohedral atoms is described accurately by the Einstein model [13,14]. In order to evaluate the translational energy of the endohedral  $H_2$  molecule, we have also employed the Einstein model derived from the quantized energy levels of a harmonic oscillator, with an Einstein temperature  $\Theta_E$ . This view is consistent with previous theoretical predictions [8,9] as well as the electron density map of  $H_2$  described earlier. Applying these models with one fitting parameter  $\Theta_E$ , we have calculated  $C_{fit} = C_{trans} + C_{rot}$  in Fig. 3. As seen in Fig. 3, the curve fitted with  $\Theta_E = 260$  K is in good agreement with the experimental data. We note that the deviation observed above 200 K is due to the orientational phase transition of  $C_{60}$ , which strongly depends on the crystal quality. Our analysis shows that the endohedral hydrogen molecule in  $H_2@C_{60}$  can be described as an almost isolated harmonic oscillator with quantized translational motion confined in the  $C_{60}$  framework and acts as a free rotor without ortho-para conversion.

The translational energy can also be discussed by solving the Schrödinger equation for a single particle confined in an ideal three-dimensional spherical potential:  $E_{trans}(n, \ell) = \beta_{n,\ell}^2 \hbar^2 / (2\mu r^2)$ , where  $r$  is the radius of the cavity,  $\beta_{n,\ell}$  is the  $n$ th root of the spherical Bessel function with the quantum numbers of  $n$  and  $\ell$ , and  $\mu$  is the reduced mass [5,6]. The translational energy difference between the ground and the first excited translation levels can thus be estimated from  $\Delta_{trans} = E_{trans}(1, 1) - E_{trans}(1, 0) = 10.32\hbar^2 / (2\mu r^2)$  to be  $\sim 25$  meV ( $\Delta_{trans}/k_B \sim 290$  K) with  $r = 0.65$  Å estimated from the diameter of the fullerene (7.1 Å) and the van der Waals radii of H (1.2 Å) and C (1.7 Å) [5]. The  $\Theta_E$  used to fit  $\Delta C_p$  is fairly consistent

with this translational energy and slightly larger than the translational energy of  $H_2$  ( $\sim 17.5$  meV = 200 K [Ref. [6]]) in anisotropic open cage fullerenes. Considering that the  $\Delta_{trans}$  is reduced by the increase of  $r$ , this difference can originate from the larger diameter along the two long axes of the open cage fullerene (7.3–7.8 Å) as compared to the isotropic  $C_{60}$  fullerene.

In the low-temperature region, a Schottky-like anomaly is clearly evident in Figs. 2 and 4. The entropy associated to this anomaly was calculated to be  $6.8$  J K $^{-1}$  mol $^{-1}$  and displayed also in Fig. 4(b). Since the rotational excited levels in both ortho and para spin isomers are located a few hundred Kelvin above the ground state as discussed earlier [1,5,6], we take into consideration only the lowest rotational sublevels of the nuclear spin isomers ( $J = 0$  for para- $H_2$  and  $J = 1$  for ortho- $H_2$ ). The threefold degeneracy in the  $J = 1$  level can be lifted by the energy potential in the low-temperature  $Pa\bar{3}$  phase [15,16], and such splitting is expected to produce a  $C_p$  anomaly as the one observed in our experiment. Indeed, the expected excess entropy due to the splitting of the  $J = 1$  level with 75% ortho- $H_2$  ( $0.75R \ln 3 = 6.85$  J K $^{-1}$  mol $^{-1}$ ) is quite close to the measured entropy. The ortho- $H_2$  fraction of 0.75, expected to hold in the entire temperature range [1,12], provides additional support for a forbidden ortho-para conversion in  $C_{60}$  cages. Additionally, we checked the sample dependence of the entropy and found it to be proportional to the  $H_2$  content. This fact unambiguously supports the interpretation of the anomaly in terms of rotational sublevel splitting.

We have then tentatively analyzed the rotational sublevel splitting  $\Delta E_{rot}$  of the triply degenerate  $J = 1$  levels by employing a two-level Schottky model (one ground state and doubly degenerate excited states) which can be ex-

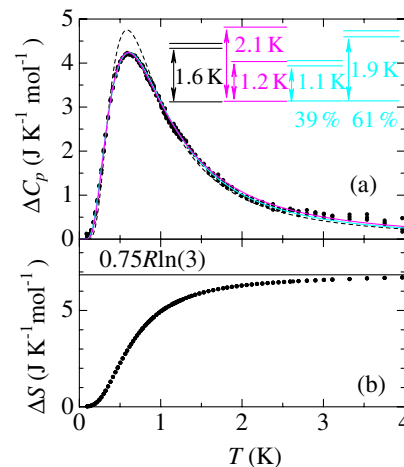


FIG. 4 (color online). Excess specific heat  $\Delta C_p$  and excess entropy  $\Delta S$  below 4 K. (a) The black dashed, magenta, and cyan curves indicate the results of two-level, three-level, and dual two-level Schottky fits, respectively. (b)  $\Delta S$  was calculated from  $\Delta C_p$ .



pected in the  $S_6$  symmetry of a  $C_{60}$  molecule in the  $Pa\bar{3}$  phase [15,16]. The best fit was achieved for  $\Delta E_{\text{rot}} = 0.14$  meV ( $\Delta E_{\text{rot}}/k_B = 1.6$  K) as shown in Fig. 4(a). Because a small disagreement remained as seen in the dashed line of Fig. 4(a), this encouraged us to apply a three-level model. A much better fit was achieved for  $\Delta E_{\text{rot}} = 0.10$  ( $\Delta E_{\text{rot}}/k_B = 1.2$  K) and  $0.18$  meV ( $\Delta E_{\text{rot}}/k_B = 2.1$  K) as displayed in Fig. 4(a). The further splitting of the  $J = 1$  level suggests that the local symmetry is slightly lower than  $S_6$  symmetry. In fact, in the case of anisotropic  $H_2$ @ATOCF, a clear three-level splitting was observed ( $\Delta E_{\text{rot}} = 1.50$  and  $2.85$  meV [6]). The magnitude of the splitting first elucidated in the present specific heat measurements shows rotational sublevel splitting much smaller than those of  $H_2$  in the open caged fullerene [6] and of similar order to those of those observed in solid  $H_2$  [1,17]. The large splitting of the rotational degeneracy observed in the open cage  $C_{60}$  is most likely caused by the anisotropic energy surface accommodating the  $H_2$  molecule, and the rotational angular momentum of the ortho- $H_2$  is quenched. In contrast, the  $J = 1$  rotational sublevel splitting is rather small in the higher symmetry of  $C_{60}$ , which allows one to treat the rotational spectrum as that of a 3D free quantum rotor.

A similarly good fit can be obtained when two types of rotational sublevel splitting in the scheme of one ground and two excited levels are used at the same time. This situation might become possible when the two types of orientation of  $C_{60}$  below 90 K are taken into consideration [10], because these orientations can lead to two different crystal fields within the  $Pa\bar{3}$  space group depending on the orientations of  $C_{60}$ . The best fit was achieved for  $\Delta E_{\text{rot}} = 0.095$  ( $\Delta E_{\text{rot}}/k_B = 1.1$  K) and  $0.16$  meV ( $\Delta E_{\text{rot}}/k_B = 1.9$  K) with fractions of 0.39 and 0.61. However, these values are far from the reported fractions of 0.165 and 0.835 [10]. An alternative possibility for explaining the small deviation from the simple two-level Schottky model is that another type of disorder induces a continuous distribution of crystal field effects. However, in our measurements, the shape of the low-temperature anomaly does not depend on the sample quality, which suggests that rotational sublevel distribution is not caused by such a disorder.

In summary, our low-temperature specific heat measurements provide the first experimental evidence for a small energy splitting of 0.1–0.2 meV in the  $J = 1$  state of the ortho- $H_2$  nuclear spin isomer. This tiny rotational sublevel splitting is likely due to  $C_{60}$  having slightly less local symmetry than  $S_6$  in the low-temperature  $Pa\bar{3}$  phase. Our detailed analysis of the excess specific heat in the intermediate energy scale suggests that the confined  $H_2$  molecule can be described as a quantized oscillator in a cage. A

single molecule or an atom endohedrally accommodated in  $C_{60}$  can be used as an ideal model compound for studying quantum dynamics, which cannot be realized in any conventional solid.

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